DEVELOPMENT OF A CERAMIC MEMBRANE FOR UPGRADING METHANE TO HIGH-VALUE-ADDED CLEAN FUELS

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INTRODUCTION

The upgrading of natural gas (which consists mostly of methane) to high-value-added clean-burning fuels such as dimethyl ether, alcohols, and pollution-fighting fuel additives is driven by the abundance of natural gas discovered in remote areas. Recently, extensive efforts have focused on both direct and indirect conversion of methane to these value-added products [1,2]. The direct-conversion route is the most difficult approach because the products are more reactive than the starting reactant, methane [3]. Indirect routes require the partial oxidation of methane to synthesis gas (syngas, $CO + H_2$) in a first stage. The syngas is then converted to upgraded products in a second stage. The most significant cost associated with partial oxidation of methane to syngas is that of the oxygen plant. In this paper, we offer a technology that is based on dense ceramic membranes and that uses air as the oxidant for methane-conversion reactions, thus eliminating the need for the costly oxygen plant. Certain ceramic materials exhibit both electronic and oxide-ionic conductivities. These mixed-conductor materials transport not only oxygen ions (functioning as selective oxygen separators), but also electrons. No external electrodes are required and such a system will operate without an externally applied potential. Oxygen is transported across the ceramic material in the form of oxygen anions, not oxygen molecules.

Recent reports in the literature suggest that ceramic membranes made of these mixed conductors can successfully separate oxygen from air at flux rates that could be considered commercially feasible. Thus, they have potential applications for improving the economics of methane conversion [4-6].

Teraoka et al. [4] showed that oxides in the La-Sr-Fe-Co-O system exhibit mixed conductivity and appreciable oxygen permeability. However, we have found that these oxides are unstable when exposed to methane at elevated temperatures and are therefore unsuitable for syngas conversion. We have developed a novel ceramic composition, namely $SrFeCo_{0.5}O_x$, that is stable in methane and that has oxygen permeation suitable for the partial oxidation of methane [7,8].

EXPERIMENTAL

Ceramic powders of composition $SrFeCo_{0.5}O_x$ were made by solid-state reaction of the constituent cation salts. Appropriate amounts of $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, and Fe_2O_3 were mixed and milled in isopropanol with ZrO_2 media for ≈ 15 h. When dry, the mixtures were calcined in air at $\approx 850°C$ for ≈ 16 h, with intermittent grinding. After final calcination, we ground the powder with an agate mortar and pestle to an average particle size of ≈ 7 µm. The resulting powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis and were also analyzed for particle-size distribution.

The powder was made into a slip containing a solvent, dispersant, binder, and plasticizer. Membrane tubes were fabricated by extrusion of the slip to an outside diameter of ≈ 6.5 mm, lengths up to ≈ 30 cm, and wall thicknesses of 0.25-1.20 mm. The tubes were sintered at $\approx 1200°C$, then characterized by SEM and XRD, and finally used in our methane partial-oxidation studies.

The tubes were evaluated for performance in a quartz reactor system, as shown in Fig. 1. The quartz reactor supports the ceramic membrane tube with hot Pyrex seals. An Rh-based reforming catalyst was loaded adjacent to the tube, and a gold wire mesh was wrapped around the tube to prevent solid-state reactions between the catalyst and the ceramic tube. Both the feed gas (generally 80% CH_4 and 20% Ar) and the effluents were analyzed with a gas chromatograph. Inside the membrane tube, air was the source of oxygen.
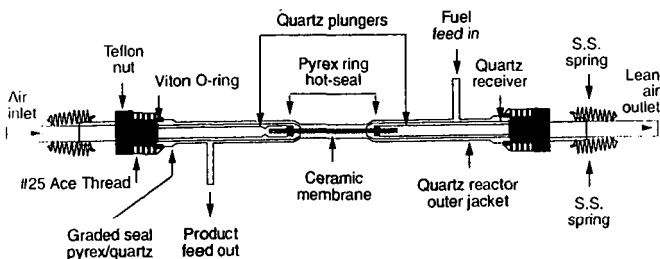
Fig. 1. Schematic diagram of ceramic membrane reactor.

Electrical conductivity was determined by a four-probe method that used a blocking electrode of yttria-stabilized zirconia (YSZ) for oxygen ion conduction [9], while the oxygen diffusion coefficient was measured by a time relaxation method. The sample was subjected to a sudden increase in oxygen partial pressure, and ionic conductivity was monitored as a function of time and temperature [10].

RESULTS AND DISCUSSION
The XRD pattern of an $SrFeCo_{0.5}O_x$ sample recorded at 850°C in an Ar-O_2 gas mixture is shown in Fig. 2. The material exhibited remarkable structural stability at high temperature, and no phase transition was observed as oxygen partial pressure was changed. This structural stability of $SrFeCo_{0.5}Ox$, when compared with that of other mixed conducting oxides of similar type, is reflected in its physical and mechanical properties, as shown in our earlier publications [7,11].

The measured electronic and ionic conductivities of $SrFeCo_{0.5}O_x$ and other materials of the same family are shown in Table 1. It is clear that this material is unique in that its ratio of ionic to electronic conductivity is close to unity. The chemical diffusion coefficient, as determined by the conductivity relaxation method [9], is shown in Fig. 3. The diffusion coefficient increases exponentially with temperature, and at 900°C, is $\approx 9 \times 10^{-7}$ cm²/s. Activation energy associated with oxygen diffusion is ≈ 0.9 eV, which indicates that oxide ions can move more easily in the $SrFeCo_{0.5}O_x$ sample than in other mixed-conducting oxides.

Figure 4 shows conversion data obtained with an $SrFeCo_{0.5}O_x$ membrane tube operated at 850°C for ≈ 70 h in the reactor setup shown in Fig. 1. As seen in Fig. 4, methane conversion efficiency is >98% and CO selectivity is $\approx 90\%$. Measured H_2 yield is about twice that of CO, as expected.

Observations by Liu et al. [12] indicate that not only the conductivity of the membrane material, but also the catalytic activity of the surface or interfaces, has a significant effect on the rate of oxygen permeation. Conductivity (ionic and electronic) determines the mass and charge transport rates through the membrane, while catalytic activity controls the rate of interfacial electrochemical reactions. To decouple the role of the catalyst in oxygen transport across the membrane, an $SrFeCo_{0.5}O_x$ tube was tested without the reforming catalyst. The results from a run of ≈ 350 h are shown in Fig. 5. The feed gases are the same as earlier (80% CH_4 and 20% Ar). In the absence of a catalyst, the oxygen that was transported through the membrane reacted with CH_4 to form CO_2 and H_2O. As seen in Fig. 5, methane conversion efficiency was $\approx 35\%$ and CO_2 selectivity was $\approx 90\%$.

Further confirmation of the stability and high performance of this membrane tube is shown in Fig. 6, which illustrates reactor results over a period of 1000 h. The feed during this period was a typical mixture expected in a commercial recycling feed, namely CH_4, CO, CO_2, and H_2. Throughout the run, methane conversion was high. A small decline in oxygen permeation was observed. The high oxygen flux is consistent with the high diffusion coefficient of 9×10^{-7} cm² s⁻¹ that was measured by the time-relaxation method [9].

Table 1. Electronic and ionic conductivities of various mixed oxides

| Sample	Electronic σ_{el} ($S \cdot cm^{-1}$)	Ionic σ_i ($S \cdot cm^{-1}$)	Method for Measuring σ_i
$SrFeCo_{0.5}O_x$	10	7	4-terminal, YSZ electron block
$SrFe_{0.8}Co_{0.2}O_x$	76	4	4-terminal, YSZ electron block
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	300	0.01	4-terminal, YSZ electron block
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	300	0.003	2-terminal, electron block
$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$	600	15	4-terminal, YSZ electron block
$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$	250	0.10	4-terminal, YSZ electron block
$La_{0.75}Sr_{0.25}FeO_3$	50	0.03	$^{18}O/^{16}O$ exchange
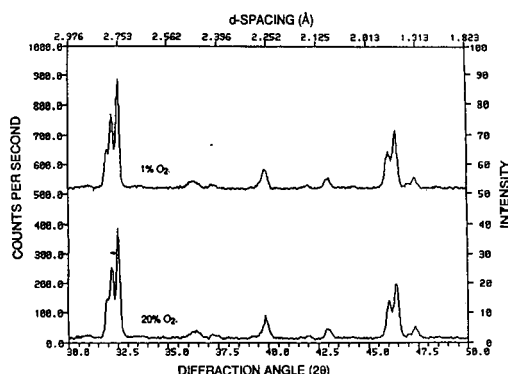
Fig. 2. XRD of $SrFeCo_{0.5}O_x$ at 850°C in 1% and 20% O_2 (balance is Ar) atmosphere.
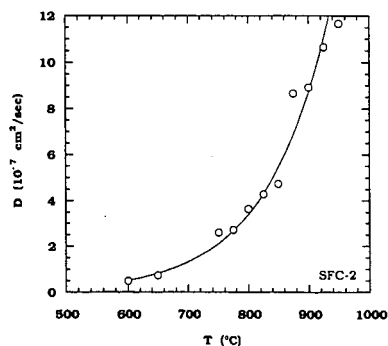

Fig. 3. Chemical diffusion coefficient in $SrFeCO_{0.5}O_x$ as a function of temperature.
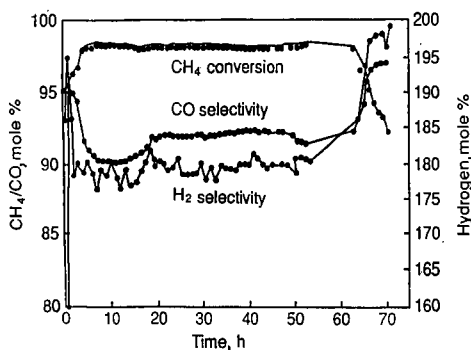
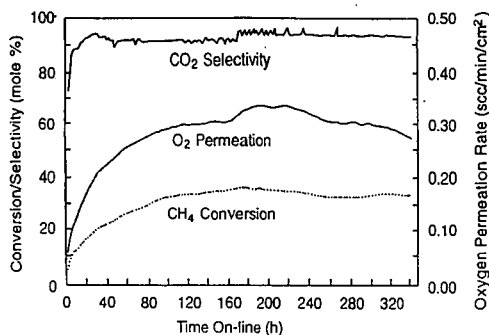Fig. 4. Methane conversion and CO and H_2 selectivity in $SrFeCo_{0.5}O_x$ membrane reactor with reforming catalyst.

Fig. 5. Methane conversion, CO_2 selectivity, and O_2 permeation in $SrFeCo_{0.5}O_x$ membrane reactor without reforming catalyst.
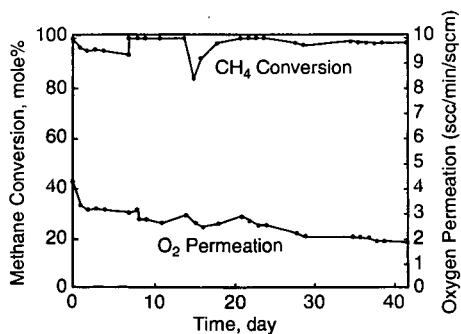
Membrane Performance Mixed Fuel Feed

Fig. 6. Methane conversion and O_2 flux for a mixed feed in $SrFeCo_{0.5}O_x$ membrane reactor with reforming catalyst.

To use the $SrFeCo_{0.5}O_x$ membrane tube in converting methane to syngas, it appears critical to reduce the tube wall thickness. Once this is achieved, any oxygen lost from the lattice of the membrane material to the reaction stream can be replaced by the oxygen permeating from the air side at a faster rate. As a result, the material in contact with the reaction stream will not be lost by chemical decomposition. Meanwhile, the difference in oxygen content between the inside and outside surfaces of the tube becomes smaller and consequently, fracturing of the tube is less likely. Thus, a thin-wall membrane tube appears to be more promising for methane conversion in the future. A thin-wall tube will also maximize the surface-area-to-volume ratio and thereby reduce the reactor size. Several suggestions have been made for manifolded monolithic systems of the type reported by Hazbun [13]. In the area of solid-oxide fuel cells, several monolithic designs have been suggested and demonstrated [14-16]; these could be adapted for use in a monolithic reactor.

CONCLUSIONS

We have developed a mixed-conducting ceramic material of the composition $SrFeCo_{0.5}O_x$ that selectively separates oxygen from air. The separated oxygen is then utilized for partial oxidation of methane into syngas. Long tubes of $SrFeCo_{0.5}O_x$ membrane have been fabricated by plastic extrusion. Performance of the membranes has been evaluated in a methane conversion reactor, and excellent methane conversion efficiency (>98%) and good CO selectivity (≈90%) were obtained in reactors run for >1000 h at 900°C. These ceramic membranes operate without electrodes or external power supply.

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